A STUDY OF SURFACE ORIENTATION

BY
JAMES VANCE ROBINSON
B.A., Pomona College, 1936

AN ABSTRACT OF A THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1940

URBANA, ILLINOIS
1940

A STUDY OF SURFACE ORIENTATION

BY
JAMES VANCE ROBINSON
B.A., Pomona College, 1936

AN ABSTRACT OF A THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1940

URBANA, ILLINOIS
1940

ACKNOWLEDGEMENT

The author is indebted to Dr. George L. Clark for the suggestion of the problem and his continued interest and advice in its development.

Thanks are due to Dr. S. T. Gross and Dr. J. N. Mrgudich for advice and help on the experimental work.

A STUDY OF SURFACE ORIENTATION

PART I

Floating Monomolecular Films

I. *Introduction*

The experimental work described furnishes evidence from which may be deduced the orientation in monomolecular films of certain substituted straight chain methyl esters upon a water surface. The interest in the problem was inspired by the need in the oil industry to know the mechanism of action of certain polar organic compounds, which, when added to a lubricating oil, increase its "oiliness." Of the various theories of this mechanism, the one considered in this investigation is that the addition agent is adsorbed on the metal, acting as a buffer between the metal surfaces. X-ray diffraction has previously been used in this laboratory to show that such an adsorption actually takes place.[3,4]

The monomolecular film balance was selected as a tool to furnish quantitative data on the strength of adsorption, and the nature of the molecular packing of materials used as "oiliness" agents. It is suggested that the collapse-pressure of monomolecular films, measured on the hydrophil balance, may be correlated with the resistance to shear of the same substances oriented on a metal surface in an engine bearing. It is also suggested that a surface consisting of a close-packed array of hydrogen atoms, attached to hydrocarbon chains, should offer the minimum hindrance to the hydrocarbon molecules of a lubricating oil slipping over it.

The history and development of the hydrophil balance have been described recently in the literature.[1,7] The fundamental principles governing the interpretation of data from the hydrophil balance are the Principle of Short Range Forces, the Principle of Independent Surface Action, and stereochemical considerations.[7]

II. *Apparatus*

The apparatus consists of the film balance[11] set in a large air thermostat, with controls permitting manipulation of the barrier de-

termining the area, and the torsion head measuring the pressure, from outside of the case. The toluene-expansion thermoregulator is immersed in the water of the trough, maintaining the temperature of the water constant within one-half degree. A detailed technic for making the determinations was worked out.

III. *Experimental Results*

The series of compounds studied was the methyl esters of certain substituted, eighteen carbon, straight chain fatty acids. The compounds are: methyl stearate, ethylene glycol distearate, methyl oleate, methyl ricinoleate, methyl 9, 10-dichloro-12-hydroxystearate (chlorinated methyl ricinoleate), and ethylene glycol ricinoleate. Tricresyl phosphate is reported incidentally. The purity of any of these compounds is questionable, but the results are qualitatively consistent with the structural formulas.

The apparatus is capable of good precision, but it is found that the monomolecular films have a greater or lesser degree of reproducibility which is characteristic of the substance in the film.[6] The variations in results may therefore be very large or very small, dependent upon the compound.

The experimental results are summarized in Tables I and II.

TABLE I

Films on Pure Water

	Temp. °C	Number Detmns.	Area at Zero Compression	Av. Dev. from Av. -Percent	Collapse Pressure Dynes per Cm.
Methyl Stearate	30	7	30.4	4.08	20.
	25	2	26.3	0.96	
Methyl *alpha*-Chlorostearate	30	8	55.1	3.3	13.
	25	2	53.3	6.11	
Methyl Dichlorostearate	30	3	62.7	5.05	12.5
	25	4	59.8	1.96	
Methyl Oleate	25	3	52.0	3.5	14.5
Ethylene Glycol Distearate	30	6	49.5	2.52	19.
	25	1	51.		
Methyl Ricinoleate	30	11	147.8	2.90	19.
	25	3	131.6	0.19	
Chlorinated Methyl Ricinoleate	30	5	113.7	0.38	10. (?)
	25	2	113.0	0.44	
Ethylene Glycol Ricinoleate	30	5	253.	4.23	16.5
Tricresyl Phosphate	30	5	111.8	2.55	10.5
	25	2	111.0	0.0	

TABLE II

Films on Chlorine Water

Substance	Temp. °C	Time Before Compression Minutes	Area at Zero Compression	Collapse Pressure
Methyl Stearate	25	10	29.0	36.
	25	3	29.0	
	25	3	29.5	
Methyl Oleate	25	10	104.	19.
	25	15	109.	
	25	20	118.	
Methyl Ricinoleate	25	10	145.	12.5
	25	15	154.	
	25	20	171.	

IV. *Discussion of Results*

The area per molecule assumed by methyl stearate on the water surface is nearly doubled by the presence of one chlorine atom in the chain (methyl *alpha*-chlorostearate) and further increased by the presence of two chlorine atoms (methyl dichlorostearate). The stability of the films of the chlorinated esters is less than that of methyl stearate. Calculations show that the increased area may be accounted for approximately by the bulk of the chlorine atoms.

The *cis* configuration of the olefinic linkage in methyl oleate prevents the molecules from packing into a condensed film of the methyl stearate type.[9]

The hydrophilic character of those compounds containing hydroxyl groups can be satisfactorily explained by the assumption that inter- or intramolecular hydrogen bonding between two hydroxyl groups decreases their hydrophilic character as compared with a hydroxyl group in contact with the water only.[8,9]

With methyl ricinoleate, intermolecular hydrogen bridge formation is prevented by the *cis* configuration, hence the molecule is strongly

hydrophilic at two points along its length. Hydrogen bonding evidently occurs between adjacent hydroxyl groups in chlorinated methyl ricinoleate, as indicated by the decrease in hydrophilic character from methyl ricinoleate.

The addition of hypochlorous acid to the double bonds of methyl oleate and methyl ricinoleate was studied by spreading these compounds upon an aqueous solution of chlorine in the film balance trough.

Methyl 9-chloro-10-hydroxystearate, formed by the addition of hypochlorous acid to a monomolecular film of methyl oleate, gives the same type of pressure-area curve as found for methyl ricinoleate. Apparently, addition of the hydroxyl group at the surface prevents it from forming other hydrogen bonds. Methyl 9-chloro-10, 12-dihydroxystearate formed by the addition of hypochlorous acid to a monomolecular film of methyl ricinoleate, has the same type of curve as chlorinated methyl ricinoleate. This is interpreted as due to intramolecular hydrogen bonding between the two hydroxyl groups.

Ethylene glycol ricinoleate and ethylene glycol distearate have the same shape of curves and approximately twice the area per molecule as their respective methyl esters.

Tricresyl phosphate is less hydrophilic than the other compounds studied, and is apparently held to the water surface only by the unsaturated oxygen atom. This is indicated by the observation that triphenyl phosphite is as hydrophobic as a hydrocarbon.

PART II

Built-Up Films

I. *Introduction*

The built-up film technic, originated by Blodgett[2], was used in an attempt to correlate the arrangement of molecules on a water surface and a metal surface, and in the solid crystalline structure. The importance of such a correlation is to permit the use of the film balance data to predict the molecular arrangement preferentially assumed on a metal surface.

II. *Apparatus*

To the film balance was added a mechanical device for dipping solid slides through the water surface[5]. The film balance proper was not modi-

fied in any way. The barrier of the film balance was advanced to maintain any desired pressure on the monomolecular film during the dipping of the slide. This mechanical technic replaces the conventional "piston oil" and flexible barrier technic.

III. *Experimental*

The effects of the nature of the backing material, the compression of the monomolecular film, the rate of dipping and the temperature upon the ability of the films to be picked up were studied. Certain generalizations may be made in regard to preparing built-up films: (1) The monomolecular films on the water surface must be in the "solid condensed" state to be capable of transferring many layers to a solid backing. (2) The formation of the "solid condensed" state is favored by increase in lateral pressure and decrease in temperature. (3) The condition of the backing surface is most important. A hydrophobic surface favors film deposition. (4) The highest speed of dipping that will not excessively agitate the surface is the most desirable. For this reason, thin slides are preferred to thick ones.

Of the compounds in the series, only methyl stearate and ethylene glycol distearate formed built-up films more than two to five molecular layers thick. Even at a temperature of 10° C., the other compounds formed "liquid" films that would not pick up from the water surface.

The X-ray examination of the methyl stearate and ethylene glycol distearate confirmed the spacing found by others[10].

BIBLIOGRAPHY

1. Adam, N. K., *Physics and Chemistry of Surfaces,* Oxford at the Clarendon Press, Second Edition 1938.
2. Blodgett, K. B., J. Am. Chem. Soc. *57,* 1007-22 (1935).
3. Clark, G. L., Sterrett, R. R. and Lincoln, B. H., Ind. Eng. Chem. *28,* 1318-28 (1936).
4. Clark, G. L., Sterrett, R. R. and Lincoln, B. H., The Science of Petroleum (Oxford University Press) *1936,* 2566-2575.
5. Gregg, S. J. and Widdowson, E. E., Rev. Sci Instruments *10,* 236 (1939).
6. Harkins, W. D. and Nutting, G. C., J. Am. Chem. Soc. *61,* 1180 (1939).
7. Langmuir, I., Proc. Roy. Soc. (London) *A170,* 1-39 (1939).
8. Rideal, E. K. and Hughes, A. H., Proc. Roy. Soc. (London) *A140,* 253-69 (1933).
9. Rideal, E. K. and Marsden, J., J. Chem Soc. *1938,* 1163-71.
10. Stenhagen, E., Trans. Faraday Soc. *34,* 1328-37 (1938).
11. Technical Bulletin 102, Central Scientific Co., Chicago.

VITA

The author was born in Louisville, Kentucky, March 26, 1916. His primary education was received in the public schools of Des Moines, Iowa. His secondary education was completed in the public schools of Claremont, California, in 1932. He entered Pomona College in 1932, and received the Bachelor of Arts degree in 1936, with high honors and distinction in chemistry. He attended the graduate school of the University of Illinois from 1936 to 1940, holding a teaching assistantship in the inorganic division of the chemistry department from 1936 to 1938, and a special research assistantship sponsored by the Continental Oil Company from 1938 to 1940. The author is a member of the following professional and honorary societies: Alpha Chi Sigma, Sigma Xi and Phi Lambda Upsilon.